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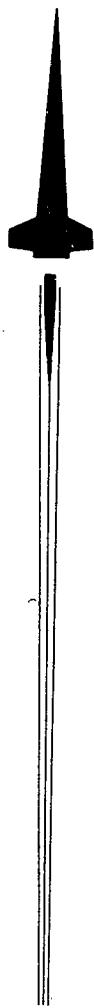


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RSIC-15

POLAROGRAPHIC METHOD OF IRON DETERMINATION IN ORES
AND SLAGS IN THE METALLURGIC INDUSTRY

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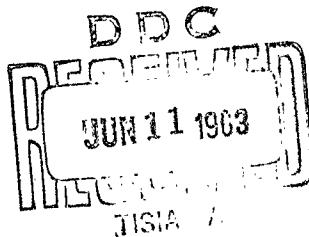
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Ingeborg V. Baker

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POLAROGRAPHIC METHOD OF IRON DETERMINATION
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by

Yu. S. Lyalikov

Several articles dealing with polarographic determination of iron have appeared in Soviet periodicals. Yu. P. Gokhstein /1/ determined iron in barium chloride, converting it into bivalent form and polarographing it in an acid medium at a potential of 1.1. S.G. Mikhlin /2/ used the same method and developed more reliable conditions than those of Gokhstein for determining bivalent iron. He specified the narrow extent of the concentration of hydrogen ions, during the presence of which it is possible to determine iron in an acid medium. In his opinion, determination is more convenient through a tartrate complex in an ammonia medium.

This method was also used by A.M. Dymov, T.D. Kubyshkina and N.S. Poli'ektova /3/.

All these authors performed determinations of iron in bivalent form after having converted it from a trivalent form by means of sulfur dioxide.

In his article Dymov noted that determination of trivalent iron was inconvenient, yet did not indicate the reasons for this inconvenience.

Analysis of iron in a trivalent ion form has been indicated in foreign literature.

During the analysis of brass, Gon /4/ determined trivalent iron in the form of a complex in an ammonia medium and obtained completely satisfactory results. Concerning this, Geirovski /5/ noted that the disadvantage of the process of determining iron in an acid medium was the possibility of a partial

reduction of iron by metallic mercury in the presence of hydrogen. However, he gave no indication on the same process performed in an ammonia medium.

Our preliminary tests with a tartrate complex of iron in an ammonia medium showed that reduction of iron does not occur even at prolonged standing of the solution in a polarizer. Polarograms of the solution taken immediately after it was poured into the polarizer and after allowing it to stand for several hours are shown in Fig. 1.

As seen from Fig. 1, the heights of the waves do not change, and thus the possibility of the reduction of iron by mercury in an ammonia medium is eliminated.

The iron may be determined in a trivalent form from the ammonia medium, appearing as a tartrate complex. Thus, we avoid the inconvenient operation of reducing iron by sulfurous gas and its subsequent elimination by hydrogen. This method was used for determining iron in ores and slags by the metallurgical industry. The work was performed by a visually read polarograph which was assembled in the laboratory of physical chemistry of the Dnieperdzerzhinskii Institute of Metallurgy.

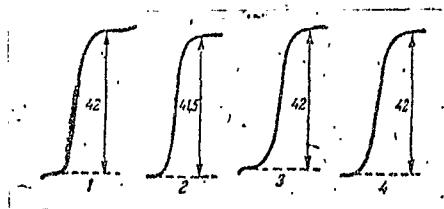


Fig. 1. Polarograms of iron in a tartrate complex at various durations of standing of the solution: 1 - immediately after the solution was poured into a polarizer, 2 - after 20 minutes, 3 - after 2 hours, 4 - after 3.5 hours

Because the wave of iron at small sensitivities $1/10 - 1/20$, especially for blast-furnace slags, was extremely small, the work was performed within the sensitivities range $1/5 - 1/3$ of the galvanometer, and sometimes even to $1/1$ (maximum sensitivity of the galvanometer $7.4 \times 10^{-9} a$). At such sensitivities the appearance of condenser currents was observed and the maximum was expressed indistinctly on the curve. For compensation of condenser currents, a polarograph circuit of Il'kovich and Semarno /5/, shown in Fig. 2, was used. The paralyzing influence of compensation on the condenser currents may be seen in Fig. 3, which also shows that during compensation the curve becomes steeper and the amplitude of oscillation of the galvanometer mirror decreases by approximately $1.5 - 2$ times less than it would without compensation.

All this considerably improves the plotting and review of the polarograms. When working with large quantities of iron, a method of compensating polarography was used, permitting work at high sensitivities of the galvanometer, although the wave of the iron exceeded the dimensions of the scale.

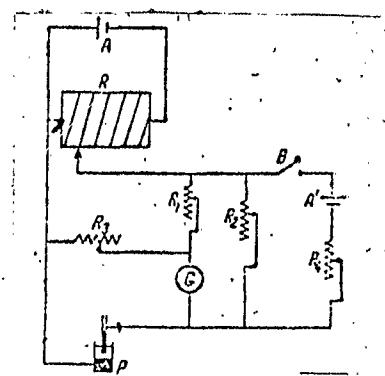


Fig. 2 A schematic drawing of a polarograph for compensating condenser currents: A - accumulator; A' - accumulator of the compensating circuit; R - Kolhraush bridge; G - galvanometer; P - polarizer; R₁ & R₂ - shunt rheostats; R₃ - rheostat for compensating currents of Il'kovich and Semarno layout; R₄ - rheostat of the compensating circuit; B - switch for engaging the compensating circuit.

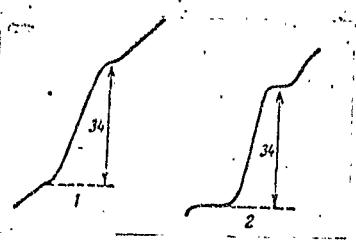


Fig. 3 Polarograms of iron, without use of the charging current condensation - 1, and with its use - 2, $S = \frac{1}{2}$

In Pavlov's /6/ recent article the relationship between the height of the wave and the concentration of the element was doubted. Therefore, it was decided that the existence of a relationship between the height of the wave and the concentration of iron of pure iron salts should be verified first, before starting determination of iron in slags and ores. The calibration curve was formed by recrystallized Mohr's salt (with 14% Fe) and pure hydroxide of iron (With 52.5% Fe). The content of iron in both compounds was investigated by permanganatometric means.

Table 1

N _{p/p.}	Soln ution ml.	Fe mg.	$S = \frac{1}{10}$		$S = \frac{1}{5}$	H_{av}
			H	$H_{\frac{1}{10}}$	$H_{\frac{1}{5}}$	average
1	1	5	3	6	5	5,5
2	2	10	4	8	9	8,5
3	3	15	8	16	15,5	15,75
4	4	20	10	20	20	20
5	5	25	12	24	26	25
6	6	30	—	—	30	30
7	7	35	18	36	33	34,5
8	8	40	19	38	39	38,5
9	9	45	21,5	43	43	43
10	10	50	—	—	47	47
11	12	60	28	56	—	56
12	15	75	35	70	68	69
13	20	100	42	84	83	83,5
14	24	120	48	95	94	95
15	26	130	51	102	100	101
16	30	150	54	108	110	109

Tests were performed as follows: 4.7619 g of hydroxide of iron were dissolved in hydrochloric acid; the iron was oxidized by Berthollet's salt to trivalence, and after elimination of chlorine, the solution was diluted to 250 ml ; attempts to oxide iron by nitric acid did not bring about the desired results as the wave of the iron was hardly distinct, due to the influence of the anion of the nitric acid entering the complex with iron; this fact was also indicated by Geirovski /5/ and Gon /4/. The obtained solution contained 5.0 mg of iron in 1 milliliter.

From the basic, prepared solution, specific contents were selected to which tartaric or citric acid was added; then this was neutralized by ammonia and polarographed, the results of which are given in Table 1 and shown in Fig. 4. Besides, the accuracy of the obtained calibration curve was verified directly by independent batches of iron hydroxide and Mohr's salt. For this purpose specific quantities of these reagents were dissolved, treated as indicated above, and polarographed.

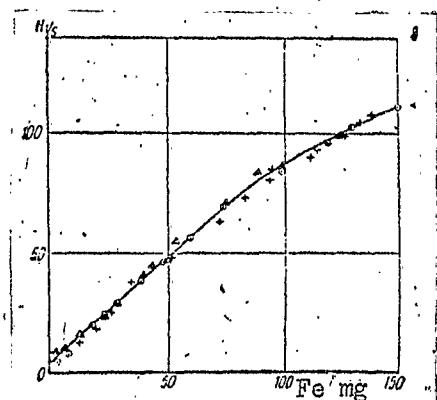


Fig. 4. Calibration curve: 0 - iron solution without foreign ions, + - iron hydroxide and Mohr's salt, Δ - iron solution with ions of calcium, manganese, aluminum.

When working with extremely small quantities of iron, it was found necessary to pass a stream of hydrogen for a period of 5 - 7 minutes through the solution for the purpose of eliminating any traces of oxygen from the solution. This caused a more abrupt wave of iron. The polarographic results are given in Table 2, and presented in Fig. 4. During analysis of slags, it was clarified that determination of iron in the form of a tartrate complex is impracticable due to polarographic distortion caused by the precipitation of insoluble tartrate calcium, which lowers the results. This may be avoided by using citric acid.

As may be seen from the results of the calibration curve that determination of iron from both complexes gives corresponding results. When analyzing the calibration curve it is imperative to note the following facts:

1. The curve does not begin from the start of the reading of the coordinate system. Gon /4/ also encountered similar conditions of the calibration curves for iron, nickel, zinc and lead.

2. With approximately 75 mg of iron, the calibration line is straight in which the height of the wave is related to the concentration shown by the equation:

$$C = A + BH$$

3. Direct proportionality between the height of the wave and the concentration is absent. (Pavlov /6/ found a direct proportionality between the height of the wave and the concentration in bivalent iron)

From the above indications it may be seen that quantitative determination of iron is completely possible by polarographic means by the height of the wave. The most convenient method of determination of the concentration by the height of the wave is the use of the calibration curve.

After ascertaining the possibility of quantitative determination of iron in an ammoniacal medium, the influence of the remaining components of the slag, calcium, manganese, and aluminum was verified on the height of the wave. For this purpose solutions were prepared containing the following amounts in 20 milliliters:

readings on	
CaCl ₂	CaO . . . 200 mg
MnCl ₂	MnO . . . 50 "
AlCl ₃	Al ₂ O ₃ . . . 50 "
HCl	4 ml

and from 2.5 to 75 mg of iron. These solutions corresponded with solutions of slags in batches of 0.5 gr with iron contents of 0.5 to 15%.

The solutions were treated as indicated above and polarographed; results are shown in Table 3 and Fig. 4. As may be seen from Table 3 and Fig. 4, the height of the wave of iron does not depend on the presence in the solution of calcium, manganese and aluminum ions. This may be explained by the fact that excessive ammonia (3 - 5 ml.) and salts of ammonia, originating from excessive hydrochloric acid (3 - 5 ml.), play a basic role during the determination of iron. Actually, by adding up approximately the concentrations of foreign electrolytes in the slag solution, we obtain the following contents:

FOR CaO - 200 mg - 0,003 M
MnO - 50 - 0,0007 M
Al₂O₃ - 50 - 0,0005 M
NH₄OH - 3-5 ml - 0,055-0,090 M
NH₄Cl - 3-5 ml - HCl - 0,035-0,060 M
from

Table 2

№ р/р	Substance	Complex	Fe mg	n										H _{1/2} aver age	
				S=1/2		S=1/8		S=1/6		S=1/10		H _{1/4}			
				H	H _{1/2}	H	H _{1/2}	H	H _{1/2}	H	H _{1/2}	H	H _{1/2}		
1	Гидроокись железа	Виннокислый . . .	20	10,5	25	10	18,5	11	—	5	10	10,5	—		
2	Соль Мора	То же	100	14,5	33	12,5	—	—	12	—	—	12,25	—		
3	Гидроокись железа	Лимоннокислый . . .	30	15,7	—	—	27,5	16,5	15,5	—	—	16,0	—		
4	То же	То же	40	21	—	—	32,5	19	19	—	—	19,0	—		
5		Виннокислый . . .	50	26,2	—	—	42	25	25	—	—	25	—		
6	Соль Мора	То же	200	28	—	—	—	—	25	—	—	25	—		
7	Гидроокись железа	Лимоннокислый . . .	70	36,6	—	—	66,5	40	37,5	—	—	37,5	—		
8	Соль Мора	То же	300	42	—	—	—	—	40	—	—	40	—		
9	Гидроокись железа	Виннокислый . . .	100	52,5	—	—	80	48	47	—	—	47,5	—		
10	Соль Мора	То же	400	56	—	—	—	—	51	27	54	52,5	—		
11	Гидроокись железа	Лимоннокислый . . .	140	73,5	—	—	—	—	63	31	62	62,5	—		
12	Соль Мора	То же	600	84	—	—	—	—	72	36,5	73	72,5	—		
13	Гидроокись железа	Виннокислый . . .	180	94,5	—	—	—	—	81	39	78	79,5	—		
14	Соль Мора	То же	700	96	—	—	—	—	85	42	84	84,5	—		
15	Гидроокись железа	•	190	99,5	—	—	—	—	85	43	86	85,5	—		
16	Соль Мора	•	800	112	—	—	—	—	89	—	—	89	—		
17	Гидроокись железа	•	120	115,5	—	—	—	—	90	47	94	92	—		
18	То же	Лимоннокислый . . .	240	127	—	—	—	—	95	49	98	96,5	—		
19	Соль Мора	То же	900	133	—	—	—	—	103	—	—	103	—		
20	Гидроокись железа	•	260	138	—	—	—	—	106	53	106	106	—		
21	То же	•	300	157	—	—	—	—	110	—	—	110	—		

(Note: translation of Nos. 1, 3, 4, 5, 7, 9, 11, 13, 15, 17, 18, 20, 21 in the "Substance" column is Iron hydroxide. Nos. 2, 6, 8, 10, 12, 14, 16, 19, is Mohr's salt. In the "Complex" column, Nos. 1, 2, 5, 6, 9, 10, 13, 14, 15, 16, 17 is Tartrate, and Nos. 3, 4, 7, 8, 11, 12, 18, 19, 20, 21 is citrate.)

Table 3

№ р/р	Soil solution ml	Fe mg	S=1/10		S=1/6		H _{1/2} aver age
			H	H _{1/2}	H	H _{1/2}	
1	1	5	3,5	7	8	7,5	
2	2	10	—	—	10	10	
3	3	15	7,5	15	16	15,5	
4	4	20	10	20	21	20,5	
5	5	25	—	—	23	23	
6	6	30	14	28	30	29	
7	7	35	17,5	35	—	35	
8	8	40	—	—	40	40	
9	9	45	23	46	43	44,5	
10	10	50	—	—	45,5	45,5	
11	12	60	27	54	54	54	
12	15	75	—	—	70	70	
13	20	100	43	86	85	85,5	
14	25	125	48	96	96	96	

Thus, the concentration of ammonia and ammonium chloride exceeds the concentration of the remaining elements by 30- 50 times. Thus, it is only natural that the concentration of the above does not influence the height of the wave of iron. After these preliminary tests an immediate analysis of slags and ores was undertaken.

Polarographic determination of trivalent iron in an ammoniacal medium from tartrate and citric complexes in slags and ores may be performed by three methods.

DETERMINATION OF AN INSOLUBLE RESIDUE AND IRON IN ORE

0.5 gr of ore or slag is dissolved in 15 - 20 ml of hydrochloric acid; the solution is oxidized by Bertholett's salt and is evaporated until dry. After cooling, the dry residue is dissolved in 10 -15 ml of hydrochloric acid. The solution is diluted with hot water and filtered out into a measuring retort (during analysis of slag to 100 ml ; in analysis of ore to 500 ml). The residue is washed and calcined. To the filtrate in the measuring retort a solution of citric or tartaric acid is added (the latter only for ore) carefully so that the quantities of these acids will equal 1.5 - 2 g. The solution is neutralized by ammonia and 2 - 3 ml of its excess is added; further, it is diluted up to the marker, mixed, and then a portion of it is poured into a polarizer. For blast-furnace slags containing little iron, a stream of hydrogen is preliminarily passed through the solution for 5 - 7 minutes, after which it is polarographed.

DETERMINATION OF IRON DURING A COMPLETE ANALYSIS OF SLAG

The filtrate from under the silicic acid, obtained as indicated above, is transferred into the measuring retort up to 100 ml. A pipet extracts 2.5 ml of the solution, which is polarographed after addition to it of citric acid and ammonia. The remaining portion of the filtrate is used for determining the amount of sesquioxides, calcium and magnesium.

RAPID DETERMINATION OF IRON IN SLAGS AND ORES

0.1 g of ore or 0.5 g of slag is dissolved in 15 - 20 ml of hydrochloric acid, then oxidized by Bertholett's salt and the solution boiled until the chlorine is eliminated. The solution is transferred into a measuring retort with 100 ml capacity; then it is cooled, and citric acid and the excess of ammonia is added to it. It is then diluted up to the marker and one portion is polarographed, disregarding the presence of silicic acid residue. The determination results of iron in slags and ores are given in Table 4, which shows that the results of determination of iron in trivalent form by polarographic methods are completely satisfactory. By taking a reading of the height of the wave with precision of up to 0.5 mm, we obtain an accuracy of about 0.5 mg in the determination of iron. From here we obtain the following definitions for various materials. For a blast-furnace slag with a total content of 6 mg or 1% of iron, the relative error is 10%, the absolute 0.05%. For martensite slag with a total content of 50 mg or 10% of iron, the relative error is 1%, the absolute 0.1%. For iron ore with a total content of 50 mg or 50% of iron, the relative error is 1%,
10

the absolute 0.5%. The exact timings in minutes of the determinations of iron by the first and the third method are as follows:

	I method	III method
1. For dissolving and oxidizing a batch	5	5
2. Evaporation	5	2
3. Cooling	3	-
4. Dissolving the dry residue	5	-
5. Filtration	5	-
6. Treatment of the solution	2	2
7. Polarography and reading	5	5
Total	30 minutes	14 minutes

FINDINGS

1. A polarographic determination method is developed for determining trivalent iron in an ammoniacal medium from tartrate and citrate complexes in slags (blast-furnace and martensite) and ores.
2. The duration of iron determinations in slags and ores is reduced to 10 - 15 minutes.

TABLE 4

№	Material	№ specimen	% Fe chemical	I method		II method		III method	
				H _{1/2}	% Fe Pol. arograph- ic	H _{1/2}	% Fe Pol. arograph- ic	H _{1/2}	% Fe Pol. arograph- ic
1	Blast-furnace slag	242	0,27	4,0	0,30	—	—	3,5	0,23
2		264	0,40	5,5	0,60	—	—	5,0	0,50
3		277	0,47	5,5	0,60	5,5	0,60	—	—
4		279	0,75	6,5	0,80	—	—	6,5	0,80
5		273	0,75	6,0	0,70	—	—	—	—
6		259	1,11	7,0	1,00	7,5	1,10	—	—
7	Martensite slag	22365	6,68	31,5	6,50	31,0	6,40	32,0	6,60
8		122971	6,98	33,5	6,70	—	—	—	—
9		122733	7,65	36,5	7,60	—	—	—	—
10		96828	7,75	38,5	7,80	38,5	7,80	38,0	7,70
11		95594	8,20	41,5	8,30	41,0	8,20	—	—
12		95600	8,80	44,0	8,80	—	—	—	—
13		22365	9,43	45,5	9,60	45,5	9,60	—	—
14		106565	13,60	67,5	13,50	—	—	67,0	13,40
15	Iron Ore	17448	50,80	48,0	51,0	—	—	—	—
16		18093	56,90	50,5	57,0	—	—	—	—
17		18092	59,95	55,5	59,7	—	—	—	—
18		19012	60,80	57,0	61,0	—	—	57,5	61,5
19		19140	66,08	61,0	66,0	61,5	66,5	—	—

Submitted 26 Dec 1937

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